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TECHNICAL REPORT BRL-TR-2985

BRL

POLYETHYLENE GLYCOL-POLY(2-METHYL-5-VINYL TETRAZOLE) POLYMER BLEND (A DESENSITIZING BINDER FOR PROPELLANTS AND EXPLOSIVES)

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Miscible polymer pairs are formed with an energetic polymer, (poly(2-methyl-5-vinyl tetrazole), PMVT, and a nonenergetic polymer, polyethylene glycol, PEG, of molecular weight 1000 to 4000. This polymer blend PEG-PMVT is formed from acetonitrile solution upon removal of the solvent. The blend also precipitates when a nonsolvent, hexane, is added to a solution of PEG-PMVT in acetonitrile at or below $0^\circ C$. With PEG E1000, blends have been formed with PEG:PMVT of 1:1 to 1:1.8 by weight.

This blend has been characterized from its unique glass transition temperature, T_g, as well as formation of transparent films. Interaction between chains in the form of weak C-H..O hydrogen bonding has been identified from infrared spectroscopy.

Polymer blends are not formed with PMVT and polypropylene glycol, PPG, with methyl side chains as well as polyols with hydroxy number 3 or more. A blend is formed, however in a narrow regime of temperature with PMVT and glycidylazide polymer, GAP.

This polymer blend is found to be a desensitizing energetic binder for propellants and for plastic-bonded explosives in particular. A PBX composition containing 91 percent RDX by weight and 9 percent PEG-PMVT polymer blend has a drop-weight-impact sensitivity better than Comp B.

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1. INTRODUCTION

This study is a part of an ongoing effort within the Ballistic Research Laboratory, BRL, to improve propellants and explosives to meet the current ordnance needs. In one application, the desired product is an explosive, possessing high enough explosiveness, but having reduced sensitivity. Reduced sensitivity implies thermal stability and increased resistance to cook off and to shock initiation. Impact sensitivity measures explosiveness using the drop-weight test. Because the explosive is a composite of organic binder and crystalline nitramines, low sensitivity implies that the binder should, not only be tough, but 'soft,' especially in the impact time frame. We have found, like many other laboratories, that the sensitivity may be improved if the percent of crystalline nitramines is reduced. In order to maintain the explosiveness, therefore, the binder must have energetic functionality. Previous work at the Naval Weapons Center confirms this view. We have found that using a moderately energetic binder like poly(2-methyl-5-vinyl tetrazole), PMVT, as one of the energetic binder components, it is possible to impart such an insensitive characteristic. Furthermore, this binder is stereoirregular like polymethylmethacrylate, and has crystalline components in it, and is a solid. We were able to form a polymer blend of PMVT with a nonenergetic binder, PEG, and as the data presented in this paper show, to desensitize plastic-bonded explosives containing 88 to 91 percent RDX by weight.

When two polymers of different natures are miscible, they form a compatible mixture. In general for polymers, however, "Compatibility is the exception and incompatibility is the rule."[1] The objective of mixing during polymer blend preparation is to bring the two polymer chains to close proximity and to effect a physico-chemical interaction between the chains, facilitating the formation of an interpenetrating network. The close proximity is important because the two miscible polymer chains still reside in domains. When the domain size is small, relaxation of nonequilibrium concentration gradients is facilitated. Blending is aided by solvents, heating, or

shearing of the mixture.[2] Yet there is a limit to the fineness of the domains. A small amount of chemical interaction, such as formation of weak hydrogen bonding, goes a long way in facilitating the formation of a blend of fine domain size.

Poly(2-methyl-5-vinyl tetrazole), PMVT, has been known for over 25 years.[3] It has the following structure:
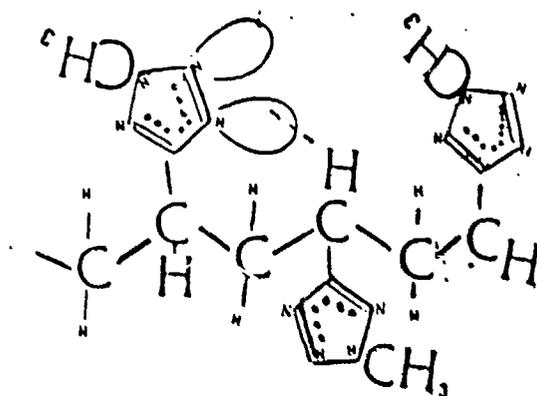
This polymer is precipitated from the monomer solution in benzotrifluoride by a free radical reaction. As shown in the experimental section, this material forms a polymer blend with polyethylene glycol, PEG. No compatible blend was formed when the chemical nature of the glycol was changed to polypropylene glycol, PPG (Polyol E-2000), or polyols of hydroxy number three or more (Dow's Voranols or BASF's Pluracols). This may be due to pendant methyl groups coming in the way of close proximity and forming a network (steric hinderance). Glycidyl azide polymer and PMVT on the other hand, formed a blend in narrow temperature and concentration regimes.

2. EXPERIMENTAL

2.1 Preparation of PEG-PMVT polymer blend. The polymer was cast in acetonitrile.[4] To a boiling solution of 3 g of PEG E-1000 (polydisperse, molecular weight 1,000), 5 g of PMVT was added slowly. The solution was stirred continuously for an additional 10 minutes after all PMVT was dissolved. The solution of the polymers was next dried slowly by spreading it over a glass plate by rolling a rod wound with wire through a puddle of the syrup. A thin, transparent noncrumbly film was formed, giving the preliminary indication that the two polymers may have formed a compatible blend. Then the solution of the polymers was cast into a flat dish, and the solvent evaporated slowly. The film formed was finally dried in a vacuum oven. The dried film was then characterized by thermal analysis, dynamic mechanical analysis, mechanical testing, transmission electron microscopy, infrared and NMR spectroscopy.[5,6,7,8]

The polymer blend was also obtained by pouring the acetonitrile-based syrup into a nonsolvent, such as hexane, which was kept cooled to between 0° to -20° C. The blend precipitated and was filtered cold.

2.2 Characterization of PEG-PMVT polymer blend.[2,3,9,10] The formation of a transparent noncrumbly film was the first indication of the formation of a compatible polymer blend, as has been indicated in the previous section. The following experimental investigations confirmed the PEG-PMVT polymer blend formation:

2.2.1 Differential Scanning Calorimetry (DSC). DSC data on the samples showed endotherms at -130° C, corresponding to transitions due to N-CH$_3$ relaxation, and at -70° C, due to the relaxation of the tetrazole ring. The main glass transition temperature of PEG was shifted upward to -4° C and a single glass transition was seen. This transition lies between -40° and

3

40° C, which is the softening temperature of PEG. The T_s-shift, calculated using the following relationship, agrees with the experimental result.[11]

$$1/T_s = W_a/T_{sa} + W_b/T_{sb}$$

where T_s = glass transition temperature of the polymer blend
T_{sa} = glass transition temperature for polymer Component A
T_{sb} = glass transition temperature of polymer Component B
W_a = # moles of a in the blend
W_b = # moles of b in the blend

2.2.2 Dynamic Mechanical Analysis. Samples of PEG-PMVT polymer blend were made by the procedure described. Before removal of all solvent, the crosslinking agent isophorone diisocyanate, IPDI, was added to cure the sample, with T-12, dibutyltin dilaurate, the catalyst. The sample cured at 70° C in 4-6 days. Polyfunctional isocyanates, such as Mobay's Mondur CB 60 PMA (trimethalol propane-TDI adduct), or Hüls polyisocyanate IPDI-T 1890/100 (isocyanurate of IPDI), were also used successfully to obtain cured PEG-PMVT. These samples show absence of moisture in DSC runs. At ambient temperature and ambient Maryland humidity, they do not pick up moisture in 30 days. The samples were repeatedly heated and cooled (100° C to 0° C); there was no shift in the DSC endotherms. Figures 1 and 2 are plots of storage modulus E', loss modulus E", and tan δ, versus temperature for cured PEG and PEG-PMVT polymer blend, respectively. When transitions or relaxations occur, there is a drop in storage modulus E', a rise in loss modulus E", and tan δ, the ratio of E"/E', shows a maxima. The DMA results confirm the T_s value from the DSC work, although they are slightly higher than those from the DSC data.

2.2.3. Measurement of Density. The density of PEG-PMVT (1.226 g/ml) was higher than the weighted average of the densities of PEG and PMVT. This is consistent with the finding of Shur and Ranby,[12] that the densities of polymer blends are about 5 percent higher than the weighted

Sample: PEG-PMVT2.02
Size: 30.2X11.8X4.3
Rate: 5 DEG/MIN
Program: DMA Modulus & Damping V2.0

Date: 14-Feb-86   Time: 12:48:53
File: PEG-PMVT2.02 DISK #1-DMA
Operator: IBM
Plotted: 14-Feb-86   15:15:25

DMA

Tensile Loss Modulus (GPa)
[----]

tan δ
[·····]

Osc Amp: 0.10

tan δ

E'

E"

Temperature (°C)

Tensile Storage Modulus (GPa)
[——]

DuPont 1790

Figure 1. Mechanical Damping Curves for PEG.

DMA

Osc Amp: 0.10

tan δ

E'

E"

Tensile Loss Modulus (Pa) [——]

[——] Tensile Storage Modulus (Pa)

tan δ [——]

Temperature (°C)

DuPont 1090
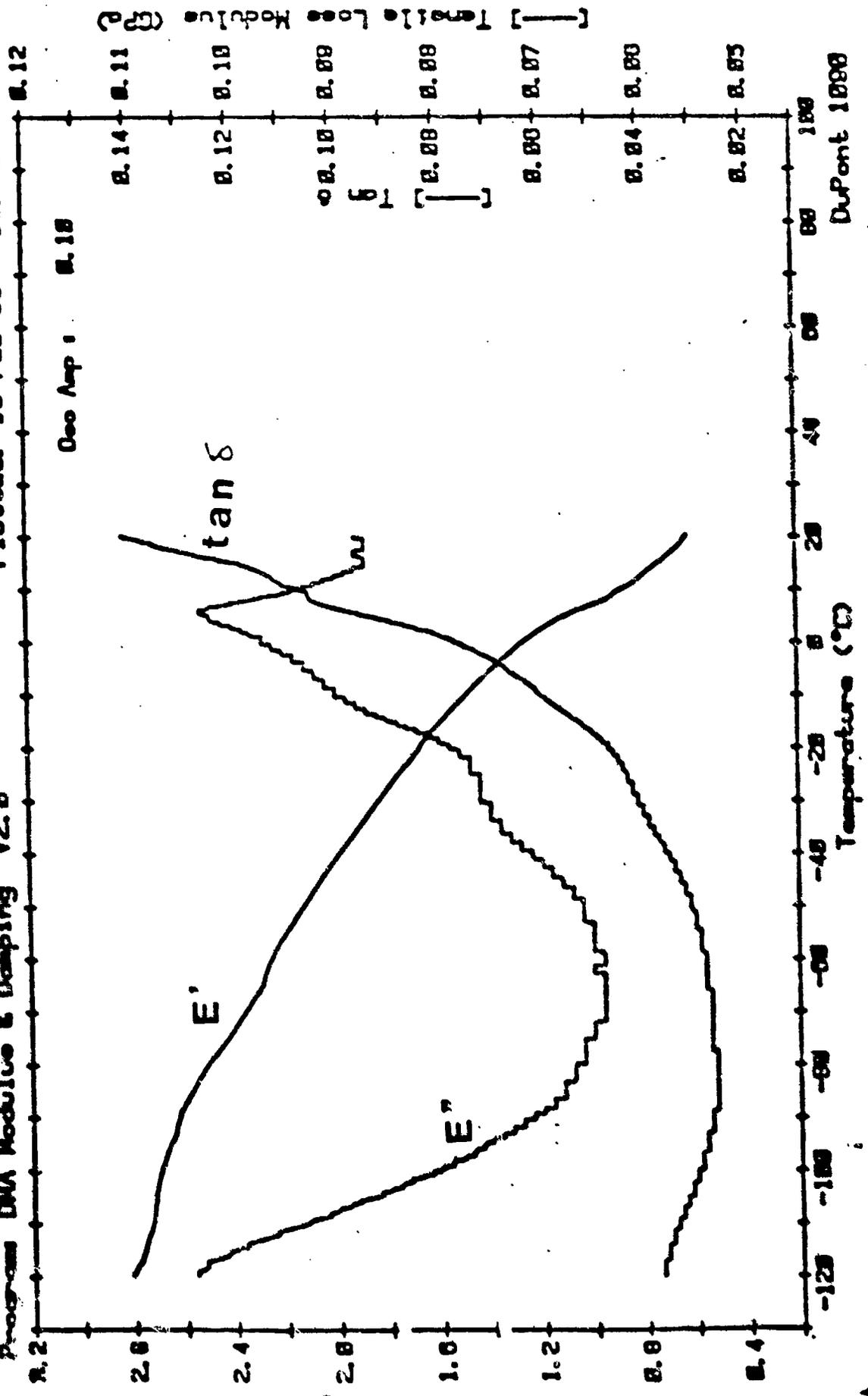
Figure 2. Mechanical Damping Curves for PEG-PMVT Polymer Blend.

average for the two components.[12] This is a desirable property because high density and good energy transfer properties are some of the requirements for a good binder for explosives.

2.2.4 Infrared Spectra of PEG-PMVT Polymer Blend.[13] The IR spectra of PEG, PMVT and PEG-PMVT polymer blends were examined, thus: Thin films of the samples were placed under a KRS-5 window, and ATR (attenuated total reflectance) spectra were taken using a Mattson Sirius 100 FTIR Spectrometer. Two-hundred scans at a resolution of 4 cm^{-1} were signal averaged and stored on a hard disc. Comparison and spectral subtraction revealed significant differences as listed below in Table 1.

Table 1. Comparison and Spectral Subtraction

Assigned Modes	PMVT, cm^{-1}	Polymer Blend, cm^{-1}
C-H vibration	2,965	2,935
Sym. C-O-C	1,060	1,040
CH bending	1,471	1,496
	1,244	1,250

In addition, there are changes in N-N and N=N vibrations as well as CN vibrations as reported for tetrazoles in the literature.[14] Figures 3 and 4 show superimposed spectra of PMVT and the polymer blend in the frequency range of 4,000 - 2,000 cm^{-1} and 2,000 - 600 cm^{-1}, respectively. Figures 5 and 6 show magnified spectra in critical regions.

2.2.5 ^{13}C and ^{1}H NMR of PEG-PMVT Polymer Blend. Tables 2 and 3 show the NMR spectrum taken in deuterated acetonitrile, of PEG, PMVT, freshly mixed PEG and PMVT, as well as the PEG-PMVT polymer blend. ^{13}C NMR spectra of freshly mixed PEG and PMVT in
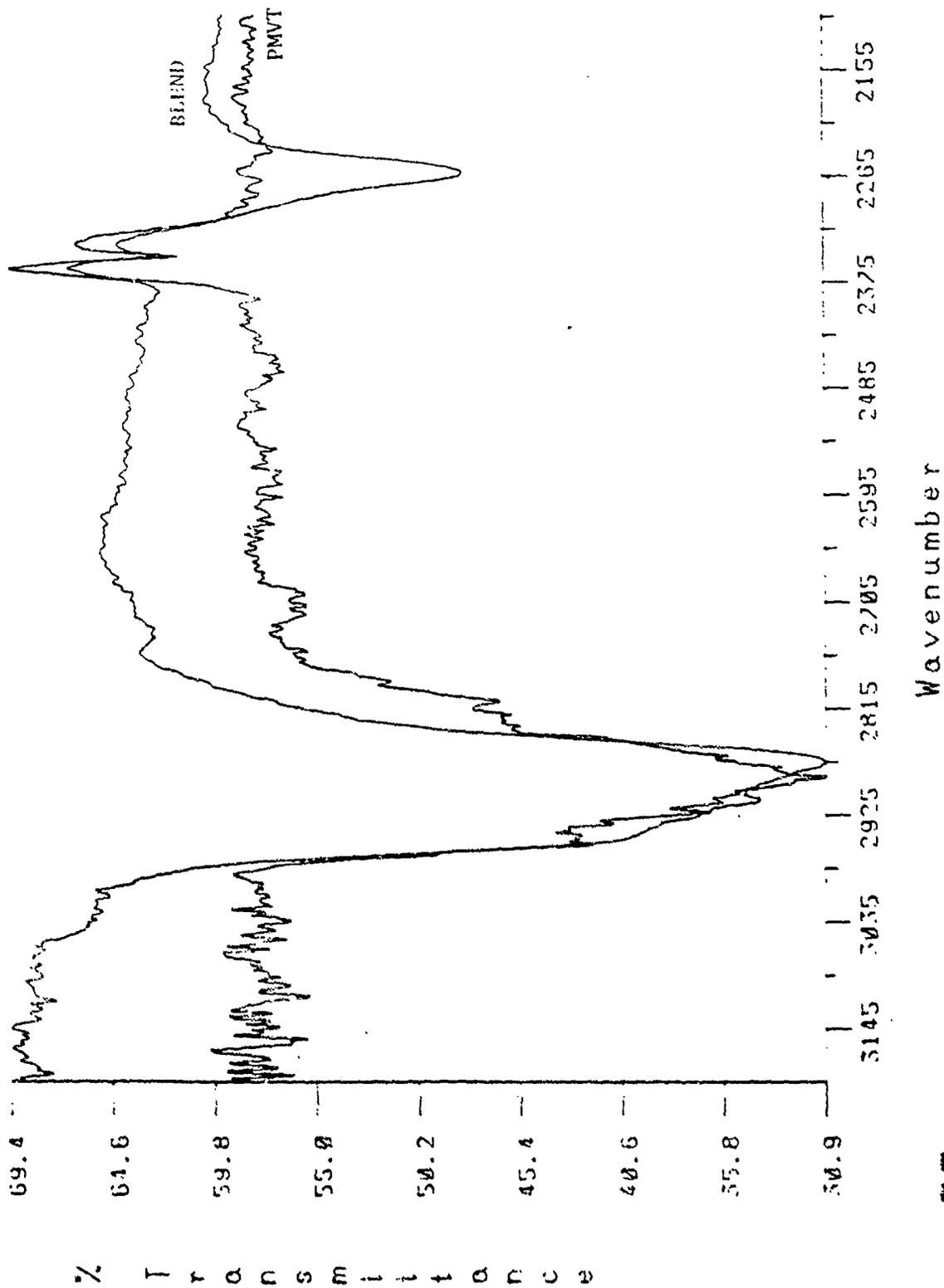
Figure 3. FTIR Spectra of PMVT and PEG-PMVT Polymer Blend (4000-2000 cm^{-1}).

peg1000-polymethylvinyltetrazole

Wavenumber

% Transmittance

8

pcp1000-polymethylvinyltetrazole

PMVT

BLEND

% T r a n s m i t t a n c e

58.2 — 51.2 — 44.2 — 37.2 — 30.2 — 23.2 — 16.2 — 9.3 — 2.3 —

2000   1720   1580   1440   1300   1160   1020   880   740   600

Wavenumber

g
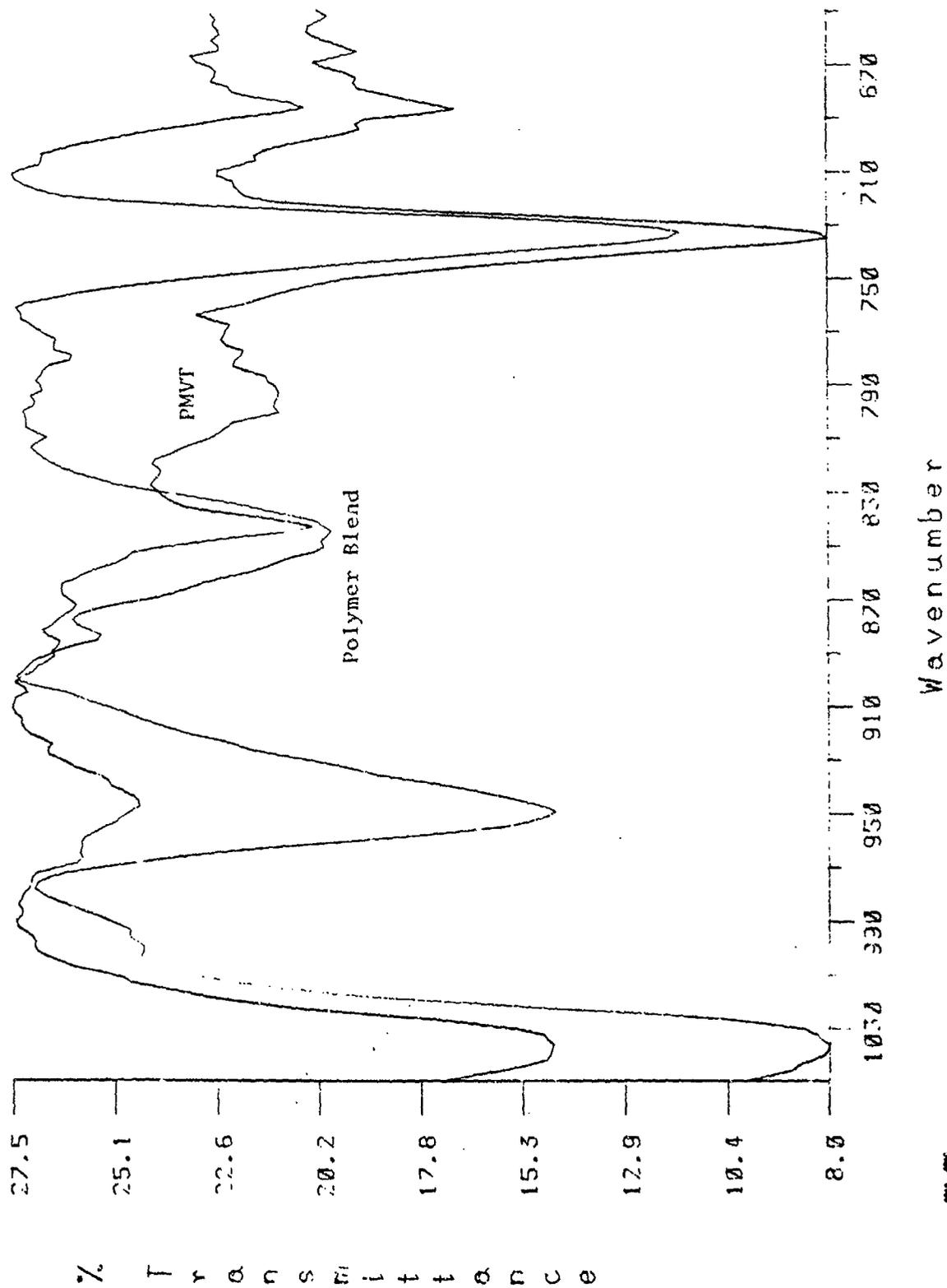
Figure 4a. FTIR Spectra of PMVT & PEG-PMVT Polymer Blend (1050-650 cm^{-1}).

reg1000-polymethylvinyltetrazole
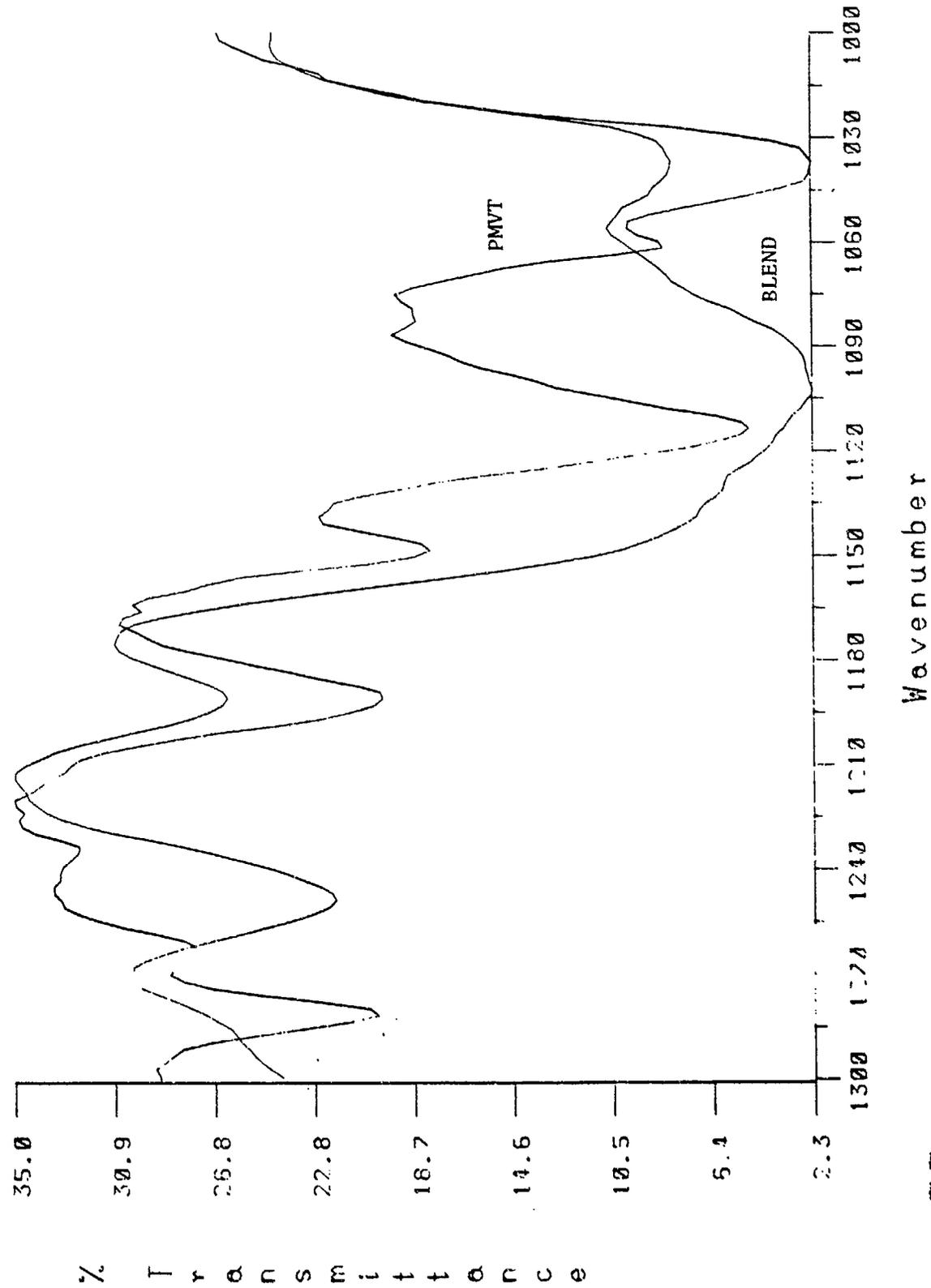
Figure 5. FTIR Spectra for PMVT & PEG-PMVT Polymer Blend (1300-1000 cm^{-1}).
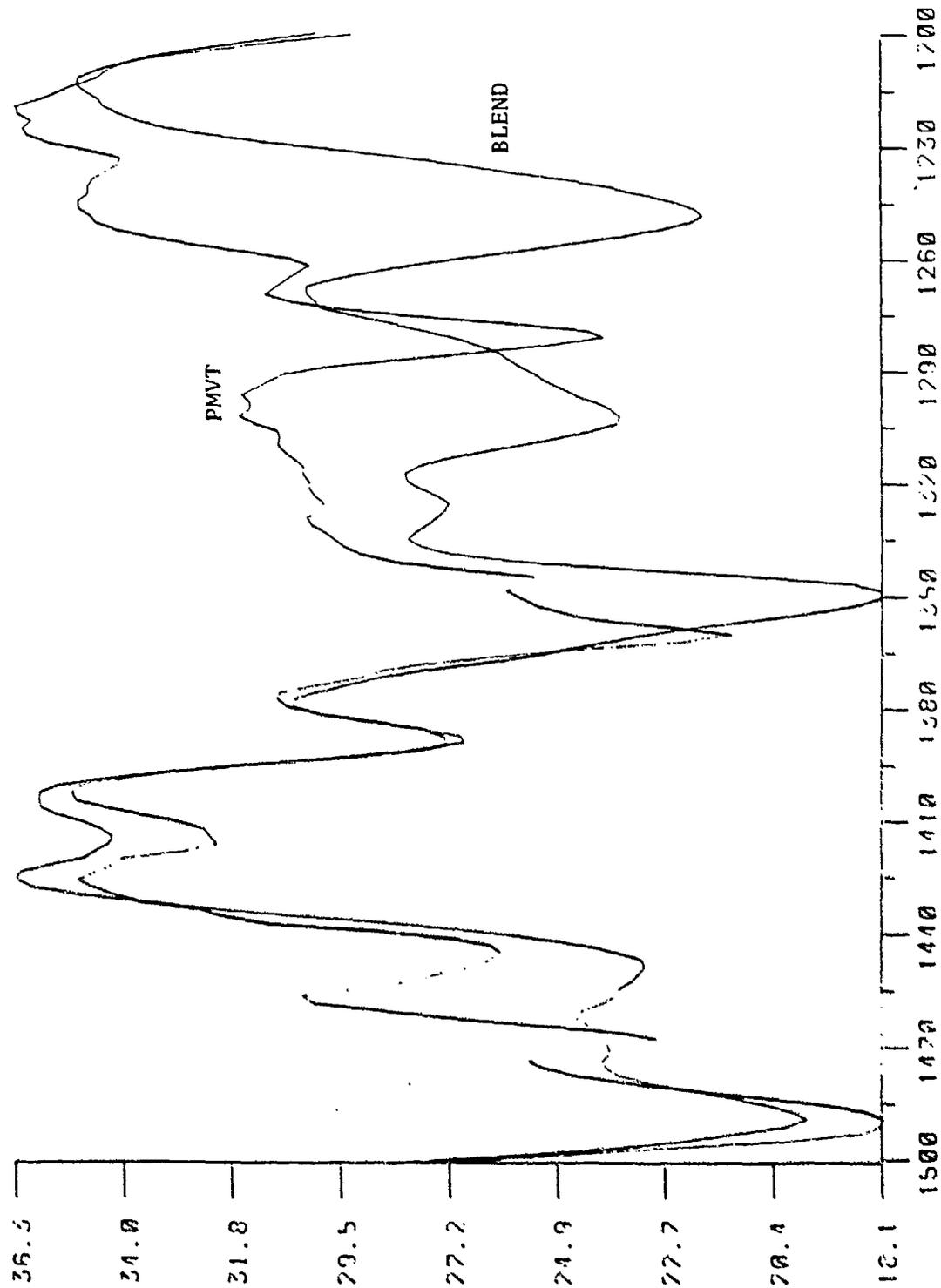
mishra-pmvt1

11

Figure 6. FTIR Spectra for PMVT & PEG-PMVT Polymer Blend (1500-1200 cm^{-1}).

peg1700-polymethylvinyltetrazole

mishra-pmvt1

12

Table I. Carbon-13 NMR Chemical Shifts

COMPOUNDS	CHEMICAL SHIFTS IN PPM
PEG	70.18
PMVT	N-CH3 31.25, CHCH2 38.07, N-C-N 167.35
BLEND	Same as the combined data for Peg & PMVT
PEG-PMVT Mixture	Same as the blend
CH3CN	117.5

Table II. 1-H NMR Chemical Shifts

COMPOUNDS	CHEMICAL SHIFTS IN PPM
CH3CN Std.	3.35 down field of TMS
PMVT	N-CH3 2.68, CHCH2 5.48, broad
Mixture	4.48, 4.18, 3.56, 3.28, 2.0
BLEND	2.04, 2.83, 4.42, 5.05, all broad

Interaction between network suggested.

acetonitrile appear to be identical to that for the polymer blend and show no change in chemical shifts (Figure 7). The proton data, on the other hand, show some changes, suggesting that some interactions exist between PEG and PMVT, especially when they interact to form a polymer blend (Figures 8 and 9). We are following the NMR of solid polymers by the magic angle spinning technique in order to understand better the nature of this interaction.

2.2.6 Examination of the Explosive Composition. PEG-PMVT polymer blend is not very energetic. The data from the Tiger code for the blend are as follows:

Density	1.21 g/mol
Heat of formation	316 cal/g
Det. pressure	60 kbar
Det. velocity	4.32 km/sec

Explosive batches were made using 91 percent RDX by weight. The remaining 9 percent consisted of the blend. The mixes were made by preparing the blend in solution, adding RDX, then removing the solvent by vacuum drying. Mixes were made with and without the curing agent. With a curing agent the 91 percent-solid loading could not be accomplished.

Impact sensitivity was measured using a type-12, drop-weight tester with a 2.5 kg drop weight [15] Table 4 data were obtained for this explosive and are compared for a few other known explosives:
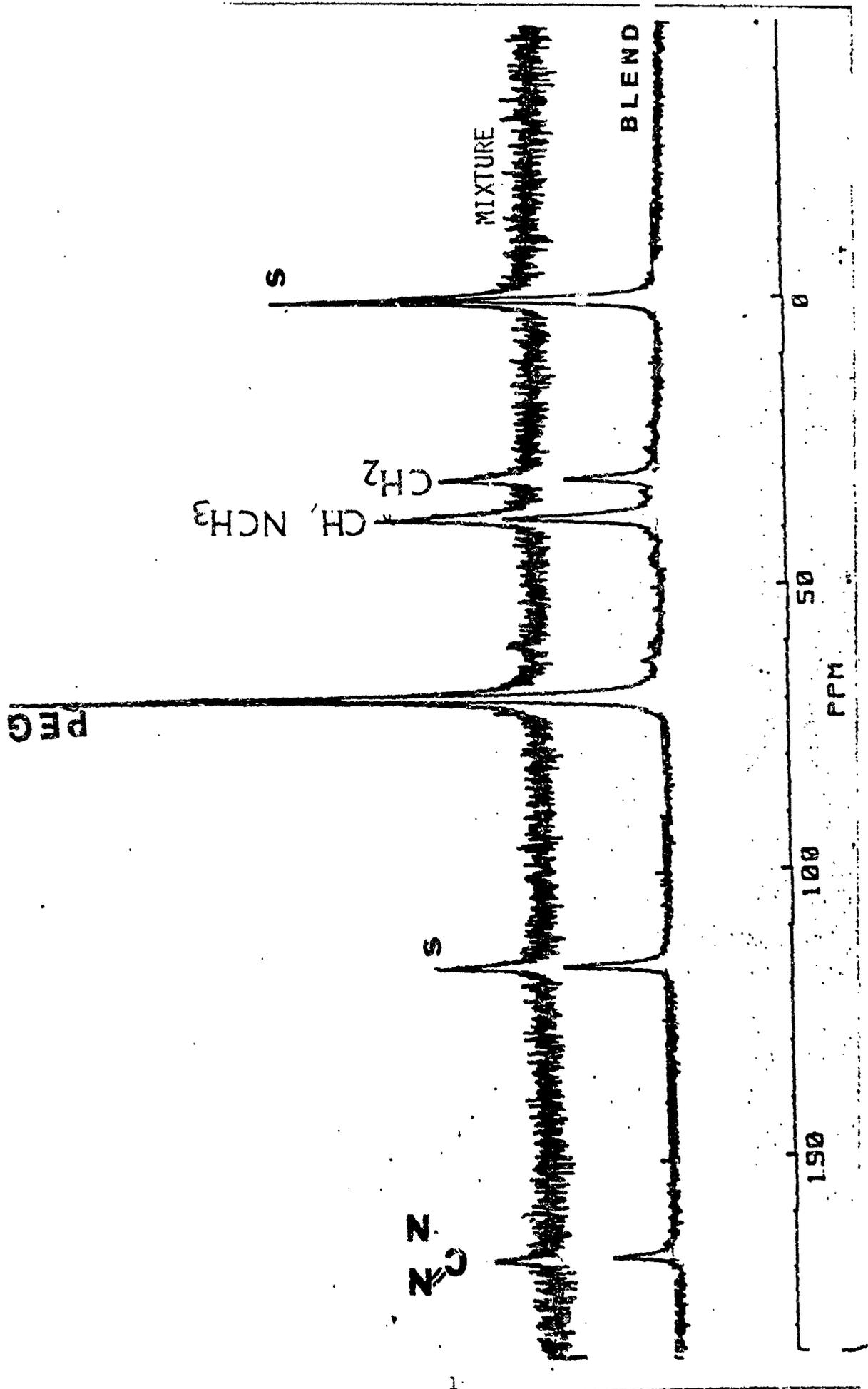
Figure 7. Carbon-13 NMR of Blend and the Mixture in Acetonitrile.
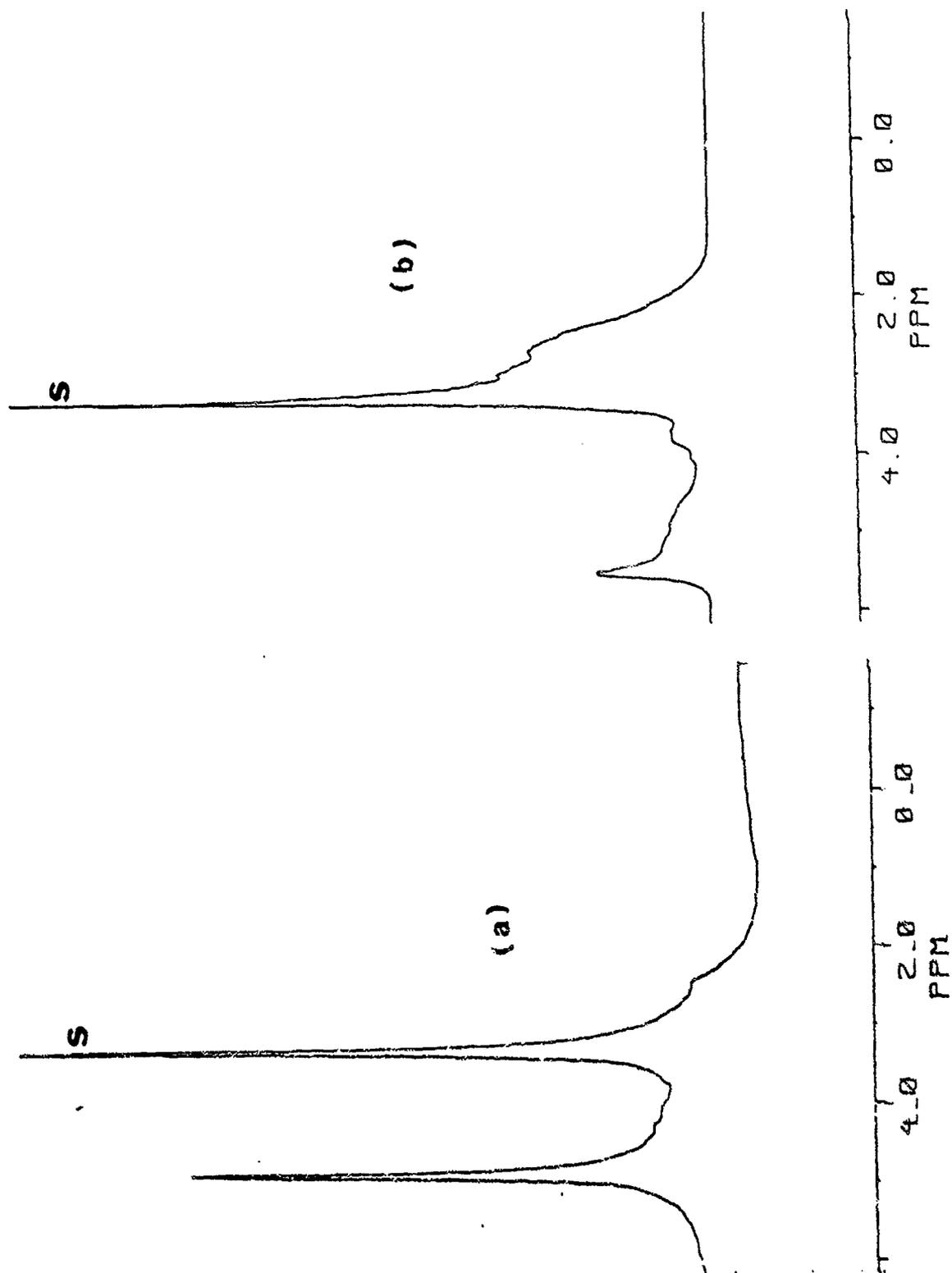
Figure 8. Proton NMR of (a) PEG, (b) PMVT in Acetonitrile.
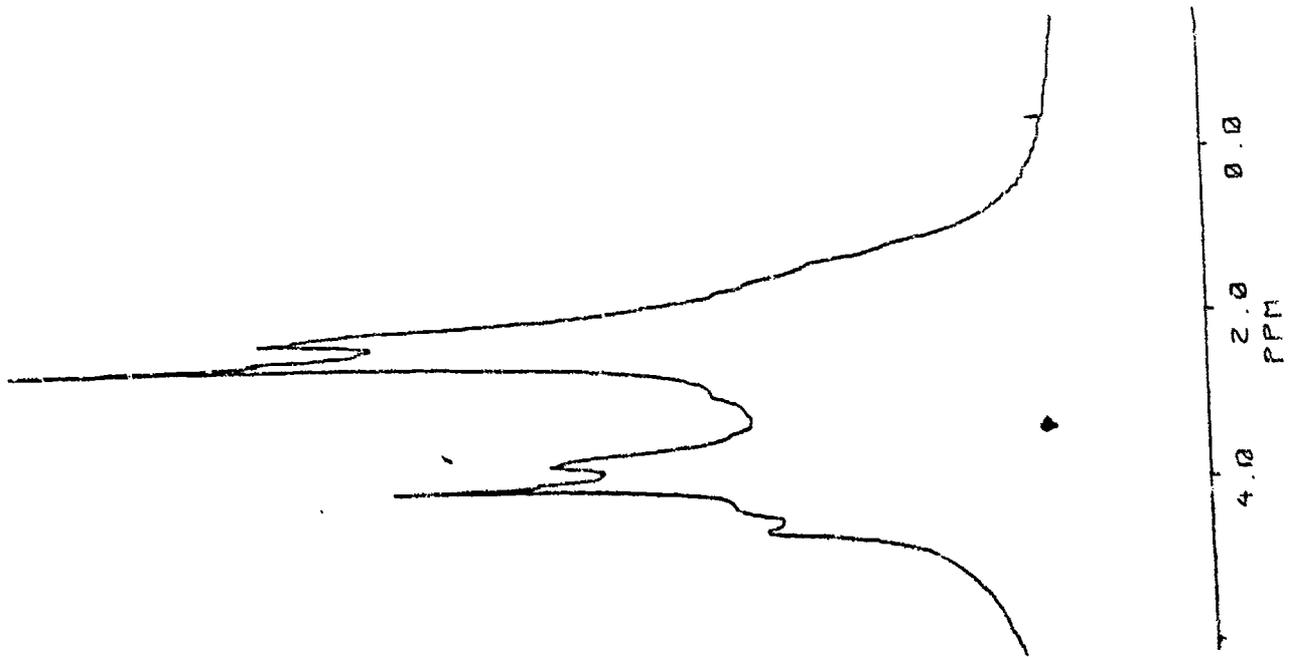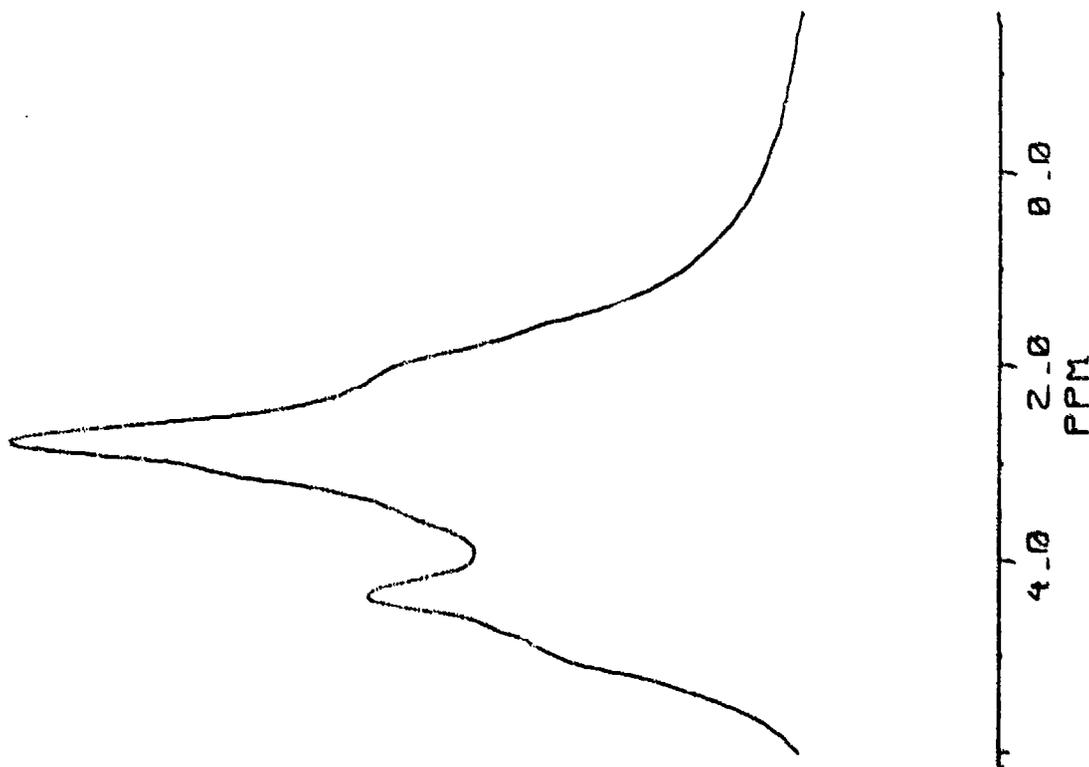
Figure 9a. Proton NMR of PEG-PMT Polymer Blend in Acetonitrile.

Table 4. Impact Sensitivity for PEG-PMVT-RDX and
Other Known Explosives

Explosives	50% point, m
TNT	1.48
A3	0.8
Comp B	0.49 - 0.8
LX-14	0.53
PEG-PMVT blend with 91% RDX	1.32

2.2.7 Blending with Other Polyols. Polymer blending was attempted with other binders. Polypropelene glycol was dissolved in acetonitrile and PMVT was dissolved into it. Upon evaporation of a dilute solution in a flat aluminum or glass dish, phase separation occurred. Unsuccessful attempts were made to form a blend with Voranol (a polyol made by Dow Chemical with hydroxy functionality 3 or more), Ethylene-propylene copolymers, EPDM, and cis-polybutadiene (Polysar). With GAF a blend was formed (transparent noncrumbly film). The blend was sensitive to formulation as well as to temperature change. A compatible blend was also formed with vinyl acetate polymer.

3. DISCUSSION

It is seen that at 91 percent RDX this explosive has an impact sensitivity of 1.32 m (versus A3 with 91 percent RDX at 0.8 m). Why should an energetic binder like PMVT reduce sensitivity?[13,16,17,18,19] Early work on the LOVA propellants by Rocchio[20] at the Ballistic Research Laboratory has shown that binders, that showed endothermic decomposition below the decomposition temperature of RDX, necessarily desensitize to thermal stimuli. The work done at

Naval Weapons Center, Naval Surface Weapons Center, and Air Force Rocket Propulsion Lab show that a 'tough' binder should generally be used for lowering sensitivity. Dr. Reed's criterion[21] for toughness of binders for plastic bonded explosives is a binder with a strain energy of >40 in-lbs/in^3. Dr. Raymond Steele of Los Alamos[22] and we at the BRL agree that a 'soft' binder is needed in order to provide a 'shock absorber' or diverter for the impact. (The term shock absorber was coined by Dr. May Chan at NWC.)

Through examining PMVT, one point becomes immediately clear.[22] The binder backbone has electron-deficient, pendant-tetrazole groups. These can act as energy sinks and absorb energy. Once they absorb energy, they may dissipate or delocalize it in many ways. For example, a tetrazole ring can absorb energy and feed it into its many π orbitals, go to an excited state and then give it off (or decompose if such is the case). Since such transitions require a specific quantum of energy, and since the molecules cannot remain long in the excited state, the energy gets delocalized. In addition, the pendant groups in a polymer backbone may undergo other vibrational transitions (known as polymer relaxations) and provide additional pathways for energy dissipation. In PMVT for example, there can be two additional such transitions: One for the tetrazole ring and the other due to the methyl side chains on the tetrazole ring. Each of these modes will need some energy to delocalize and dissipate, and that may go a long way toward desensitization

The most commonly used method for establishing polymer-polymer miscibility in blends is through the glass transition temperature, T_g, in the blends versus those of the unblended components. A miscible polymer blend will show a single glass transition between the T_g of the components with a sharpness for the transition similar to that of the components. If the miscibility is borderline, only broadening of the transition will occur. Two separate transitions between those of the constituents may result showing phases rich in either component in case of limited miscibility. When there are strong interactions, T_g may go through a maximum as a function of

concentration. All of the above are valid only when the T_g difference between components is >20° C.

One basic question, which has no universally acceptable answer today, is the level of molecular mixing required to yield a single T_g. Alternatively, the size of a "domain" or "phase" of composition in the blend needed to yield a single macroscopic property such as T_g is not well known. Kaplan,[23] from an examination of polymer morphology, has assigned a value of 150 A° as the domain size required to contain a universal segmental length associated with the glass transition. The plots from Kaplan (Figures 10 and 11) show the opaque to transparent borderline domain size and glass transition.

We have used DSC, as well as Dynamic Mechanical Spectroscopy, DMS, to determine the glass and other transition temperatures for the polymer blend. The elastic and viscoelastic properties of polymers, when subjected to small amplitude cyclic deformations, yield valuable information concerning transitions occurring on the backbone. Generally, data are obtained over a broad temperature range. In a phase-separated blend, the transition behaviors of individual components remain unaffected, whereas a single transition at a temperature intermediate between the T_g of the two components occurs for a true compatible blend. Dynamic mechanical analysis on PEG-PMVT blend shows a strong transition at 0° C, and the transition of PEG at -25° C is almost completely absent. A fine tuning of the composition PEG:PMVT may be necessary to eliminate the PEG transition in the blend altogether.

The results described here show that the polymer blend formed from PEG and PMVT are miscible in the given weight ratios at all temperatures. Hydrogen bonding seems to play an important role in strengthening the interpenetration network.

21
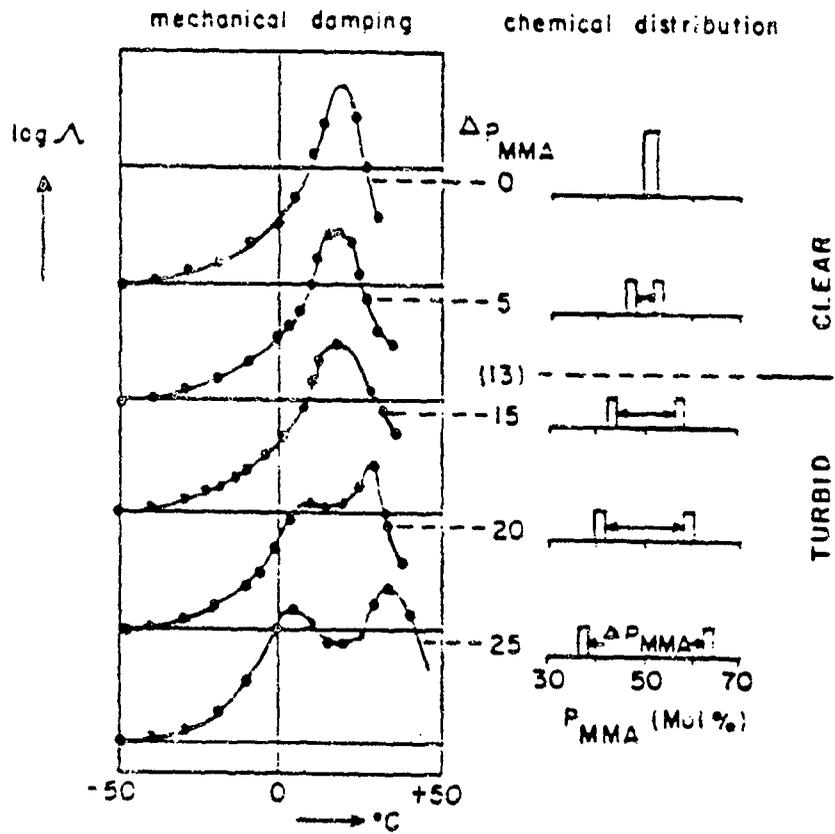
Figure 10a. Mechanical Damping Curves for PMMA-PBA Copolymers.

MOLECULAR INTERPRETATION OF T_g
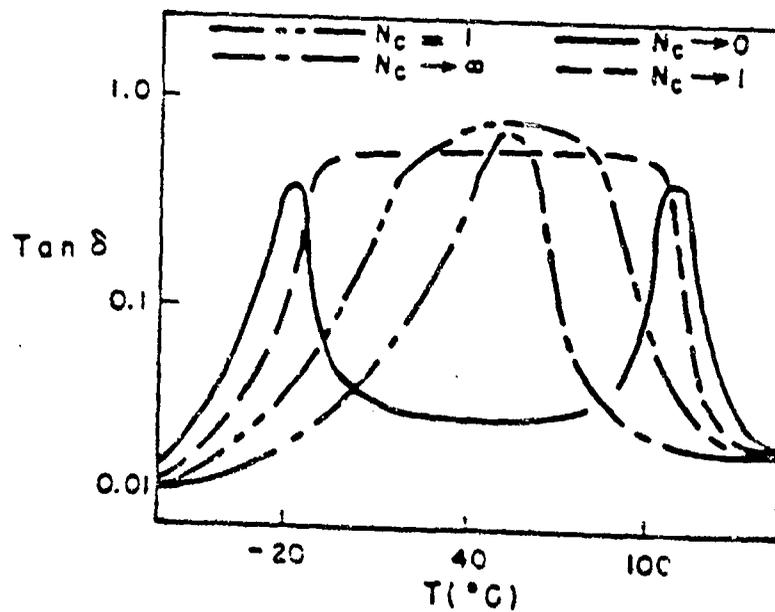
Figure 10b. Tan δ Vs. Temp. for Incompatible Systems.
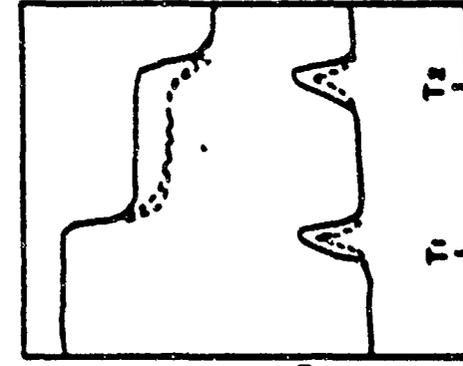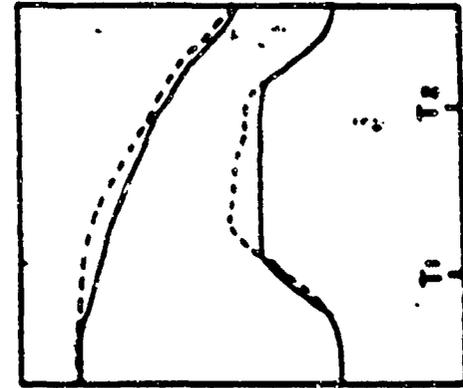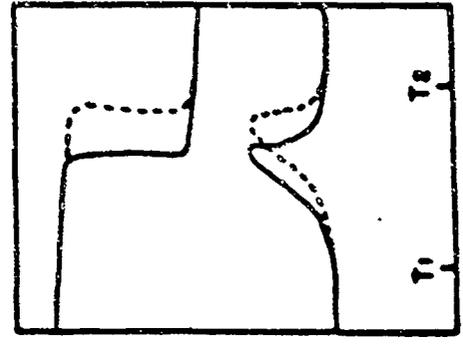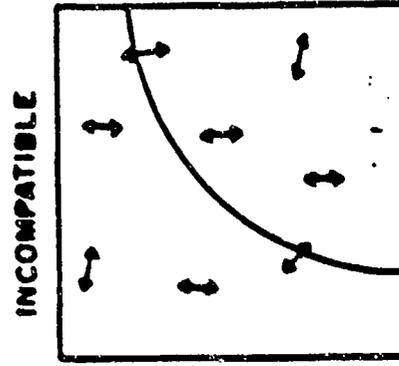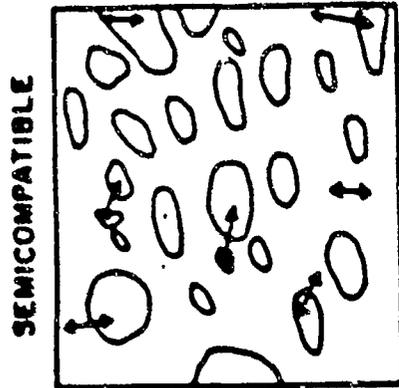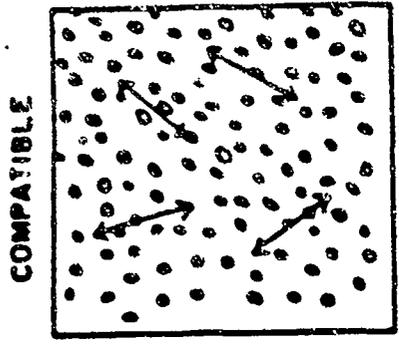
Figure 11. Mechanical Damping and Domain Size. (Kaplan)

The formation of hydrogen bonds has long been known to have a profound influence on the mode of vibration of acceptor and donor molecules involved (in this case PMVT and PEG, respectively). In the words of Pimmentel and McClellan,[24] "The vibrational spectrum provides the most sensitive, the most characteristic and one of the most informative manifestations of the hydrogen bond." For example, the C-H vibrational mode (stretch) of C_2Cl_5H, pentachloroethane, in carbontetrachloride is seen at 2,965 cm^{-1}, and it shifts to 2,895 cm^{-1} in tributylphosphine due to hydrogen bonding.[25]

2,5,8,11,14-pentaoxapentadecane polymer, $CH_3\text{-}O(CH_2CH_2O)_4CH_3$, forms a 3:1 complex with trichloromethane as evidenced from enthalpy of mixing maxima. 2,5-dioxahexane, $CH_3OCH_2CH_2OCH_3$, forms a 1:1 complex with trichloromethane, suggesting that alternate 'O' atoms of such polyethers are available for forming hydrogen bonds.[26] CH hydrogen of chloroform reacts with each nonbonding pair of electrons associated with O. In some instances, such as reported by Combelas, et al,[27] there are three modes of C-O vibration:

one due to C-O alone,

one due to $C\text{-}O..HCCl_3$, and the other due to

$$C\text{-}O \underset{\diagdown HCCl_3}{\overset{\diagup HCCl_3}{\diagup}}$$
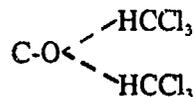
This complex should suffer from fairly severe mutual repulsion, yet the C-O stretching vibrations are found at three distinct frequencies.

The R-C-H frequencies of PMVT participating in hydrogen bonding with the O donors of PEG should show the following patterns in the IR spectra of the blends:

24

a. a shift in C-H stretching mode to lower frequency

b. an increase in the half-width of this band

c. an increase in the intensity of the band in the IR but not in the Raman

d. a shift in R-C-H bending mode to higher frequency.

Of these the $\Delta\upsilon$s is by far the most commonly utilized and reported feature taken to be characteristic of hydrogen bond formation.[25] Intensity increase is sometimes seen as a confirmation of the presence of the hydrogen bond. What is seen in the case of the PEG-PMVT polymer blend is consistent with prediction: The C-H stretching vibration is shifted from 2,965 to 2,935 wave numbers, and the bending mode is shifted to a higher frequency. It may therefore be said about the PEG-PMVT polymer blend that the active methine hydrogen of PMVT can form a hydrogen bond with the O atoms of the polyether, PEG. This provides a driving force for the formation of the polymer blend.

If we examine the NMR result, we expect the CH hydrogen resonance of PMVT to move to lower field due to H-bonding with the doner 'O' of PEG.[5,28] The H bond formation results in a small reduction of electron density of the doner molecules, and, therefore, a reduction in the shielding of its nuclei. Because the interactions are between C-H..O, the ^{13}C NMR may not show any change in chemical shifts. Indeed, there is no difference between superimposed ^{13}C NMR spectra of PEG and PMVT and the blend. The proton NMR taken in acetonitrile shows some changes, and we plan to carry out both high resolution proton NMR and magic angle spinning in the solid state for a more complete understanding of the results.[29]

One prediction can be made with regard to polymer blending with PMVT, as it possesses an active methine hydrogen. As long as hydrogen bonding can be caused by intimate contact with

other heteroatoms, such as F, O, etc., in another polymeric backbone, an interpenetrating network may be a consequence, especially in cured PEG-PMVT, barring steric factors (as we have noticed in the case of nonformation of blends between PMVT and PPG and certain polyols) and barring dispersive and polar effects. Thus, it should be possible to form interpenetrating networks between PMVT and Viton, PVC, PVA, CTBN, PBAA, PMMA, etc. As a test of this predictability, we dissolved a vinyl acetate polymer in THF, and then added PMVT, and did succeed in forming a blend. These and other results will be reported by us in due time.

4. SUMMARY

Miscible polymer pairs are formed with an energetic polymer, poly(2-methyl-5-vinyl tetrazole), PMVT of molecular weight 200,000 and with a nonenergetic polymer, polyethylene glycol, PEG, of molecular weight 1,000 to 4,000. This polymer blend, PEG-PMVT, is formed from acetonitrile solution upon removal of the solvent. The blend also precipitates when a nonsolvent, hexane, is added to a solution of PEG-PMVT in acetonitrile at or below $0°$ C. With PEG E-1000, blends have been formed with PEG:PMVT ratios of 1:1 to 1:1.8 by weight.

This blend has been characterized from its unique glass transition temperature, T_g, as well as from its formation of transparent films. Interaction between chains in the form of weak C-H..O hydrogen bonding has been identified from infrared spectroscopy.

Polymer blends are not formed with PMVT and polypropylene glycol, PPG, which has methyl side chains, or with polyols with hydroxy number 3 or greater. A blend is formed, however, in a narrow regime of temperature with PMVT and glycidylazide polymer, GAP.

This polymer blend is found to be a desensitizing energetic binder for propellants and for plastic-bonded explosives in particular. A PBX composition containing 91 percent RDX and 9 percent PEG-PMVT polymer blend has a Drop-Weight Impact Sensitivity better than that of Comp B.

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6. ABBREVIATIONS

PEG	Polyethylene glycol
PMVT	Poly(2-methyl-5-vinyl tetrazole)
DSC	Differential scanning calorimetry
TDI	Toluene diisocyanate
IPDI	Isophorone diisocyanate
IPDI-T	Isocyanurate of IPDI
Mondur CB-60	Trimethalol propane - TDI adduct
DMA	Dynamic mechanical analysis
ATR	Attenuated total reflectance
FTIR	Fourier transform infrared
EPDM	Ethylene propylene diene ter-polymer
LOVA	Low vulnerability ammunition
T_g	Glass transition temperature
δ	Chemical shift
PVC	Polyvinyl chloride
PVA	Polyvinyl acetate
CTBN	Carboxy terminated butadiene acrylonitrile
PBAA	Polybutadiene acrylic acid
PMMA	Polymethyl methacrylate
THF	Tetrahydrofuran
NMR	Nuclear Magnetic Resonance
MAS	Magic Angle Spinning
$\Delta\upsilon$	Frequency Shift
IR	Infrared

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